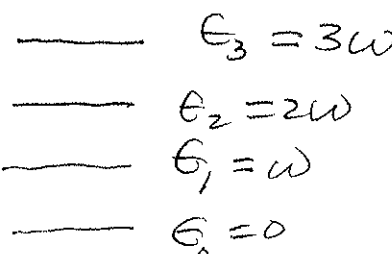


Chemistry 448

Problem Set 2

1.  $E_3 = 3w$
 $E_2 = 2w$
 $E_1 = w$
 $E_0 = 0$
- distinguishable particles
non-degenerate levels

For total energy = $3w$ the only possible distributions are:

distribution	0	w	$2w$	$3w$	No. of configurations	Probability
a	6	0	0	1	$\frac{7!}{6!1!} = 7$	$7/84$
b	5	1	1	0	$\frac{7!}{5!1!1!} = 42$	$42/84$
c	4	3	0	0	$\frac{7!}{4!3!} = 35$	$35/84$
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					Total = 84	

Distribution b is MOST PROBABLE

Same levels, still distinguishable particles but degeneracies are $g_0 = 1, g_1 = 2, g_2 = 3, g_3 = 4$

Distributions are the same but the numbers of configurations for each distribution are different:

Distribution	no. of configurations	Probability
a	$\frac{7!}{6!1!} (1)^6 \cdot (4)^1 = 28$	$28/560$
b	$\frac{7!}{5!1!1!} (1)^5 \cdot (2)^1 \cdot (3)^1 = 252$	$252/560$
c	$\frac{7!}{4!3!} (1)^4 (2)^3 = 280$	$280/560$
<hr style="width: 100%; border: 0.5px solid black;"/>		
Total = 560		<p>↑ Distribution c is most probable</p>

2. Number of possible outcomes = $(8)^2 = 64$

sum=2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
11	12	13	14	15	16	17	18	28	38	48	58	68	78	88
	21	31	41	51	61	71	81	82	83	84	85	86	87	88
		22	23	24	25	26	27	37	47	57	67	77		
			32	42	52	62	72	73	74	75	76			
				33	34	35	36	46	56	66				
					43	53	63	64	65					
						44	45	55						

54
↑

most probable is sum=9

Probability = $8/64$

3. No. of ways in which the molecules can occupy the sites is

$$W = \frac{N!}{N_A! N_B!}$$

If $N_A = \frac{N}{2} = N_B$ $W = \frac{N!}{\left(\frac{N}{2}\right)! \left(\frac{N}{2}\right)!}$

Let $N! \approx (2\pi N)^{1/2} N^N e^{-N}$

$$W \approx \frac{(2\pi N)^{1/2} N^N e^{-N}}{\left[(\pi N)^{1/2} \left(\frac{N}{2}\right)^{N/2} e^{-N/2} \right]^2} = \frac{2^{1/2} 2^N}{(\pi N)^{1/2}}$$

For $N_A = N_B = 2$ $W = \frac{4!}{2!2!} = 6$
discrepancy is 6.4%

$$W_{\text{str}} = \frac{2^{1/2} 2^4}{(\pi 4)^{1/2}} = 6.383$$

more approximate form gives $W_{\text{Avr}} \approx 2^N = 16$
 very different from 6

For $N=100$ $W = \frac{100!}{50!50!} = 1.0089 \times 10^{29}$

$$W_{\text{Avr}} = \frac{2^{1/2} 2^{100}}{(\pi/100)^{1/2}} = 1.0114 \times 10^{29} \text{ quite good}$$

only 0.25% error

More approximate form is

$$\ln N! \approx N \ln N - N$$

$$\ln 100! \approx 100(4.6052) - 100 = 360.52$$

$$\ln 50! \approx 50(3.912) - 50 = 145.6$$

$$\ln W \approx 69.32$$

$$W \approx 1.2744 \times 10^{30} \text{ (worse but still not bad)}$$

factor of 12.7 in error

4. Degeneracy of the four lowest energy levels
 i.e. $J=0, 1, 2, 3$

degeneracy is electronic $(2S+1)(10r2)$

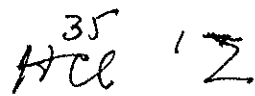
vibrational 1

rotational $2J+1$

nuclear spin $I(2I+1)$ PARA

and $(I+1)(2I+1)$ ORTHO

or $(2I_A+1)(2I_B+1)$



$2s+1=1$

$(2 \cdot \frac{1}{2} + 1)(2 \cdot \frac{3}{2} + 1) = 8$

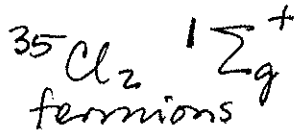
$J=0$

8×1

8×3

8×5

8×7



fermions

$J = \text{even}$ goes with

$\frac{3}{2}(2 \cdot \frac{3}{2} + 1) = 6 \text{ para states}$

$J = \text{odd}$ goes with

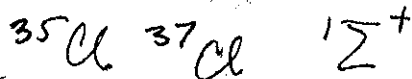
$(\frac{3}{2} + 1)(2 \cdot \frac{3}{2} + 1) = 10 \text{ ortho}$

6×1

10×3

6×5

10×7



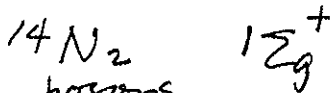
$(2 \cdot \frac{3}{2} + 1)(2 \cdot \frac{3}{2} + 1) = 16$

16×1

16×3

16×5

16×7



bosons

$J = \text{odd}$ goes with

$1(2 \cdot 1 + 1) = 3 \text{ para}$

and $(1+1)(2 \cdot 1 + 1) = 6 \text{ ortho}$

goes with $J = \text{even}$

6×1

3×3

6×5

3×7



fermions

$J = \text{odd}$ goes with

$(\frac{1}{2} + 1)(2 \cdot \frac{1}{2} + 1) = 3 \text{ ortho}$

$J = \text{even}$ goes with

$\frac{1}{2}(2 \cdot \frac{1}{2} + 1) = 1 \text{ para}$

1×1

3×3

1×5

3×7



fermions

just like $^{35}\text{Cl}_2$

6×1

10×3

6×5

10×7

	$J=0$	1	2	3
${}^7\text{Li}_2 \quad 1\Sigma^+$	10x1	6x3	10x5	6x7

because of \uparrow

$J = \text{odd}$ goes with
 $\frac{3}{2}(2 \cdot \frac{3}{2} + 1) = 6$ para states

$J = \text{even}$ goes with
 $(\frac{3}{2} + 1)(2 \cdot \frac{3}{2} + 1) = 10$ ortho

${}^{35}\text{Cl}_2 + \quad 2\Pi$	4x6x1	4x10x3	4x6x5	4x10x7
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electronic $g = (2)(2) = 4$
 fermions

$J = \text{even}$ goes with
 6 para states

$J = \text{odd}$ goes with
 10 ortho states